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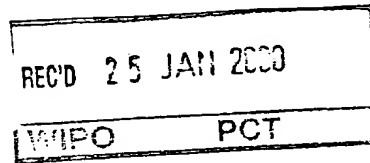


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ELECTRODE

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IAN CARMICHAEL WISHART

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## ELECTRODE

The invention relates to an improved electrode structure and specifically to a poison-tolerant electrode for fuel cells, particularly for proton-exchange membrane fuel cells.

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In a fuel cell, a fuel, which is typically hydrogen, is oxidised at a fuel electrode (anode) and oxygen, typically from air, is reduced at a cathode, to produce an electric current and form product water. An electrolyte is required which is in contact with both electrodes and which may be alkaline or acidic, liquid or solid. In solid polymer fuel cells (SPFCs), also known as proton-exchange membrane fuel cells (PEMFCs), the electrolyte is a solid proton-conducting polymer membrane, commonly based on perfluorosulphonic acid materials. These electrolytes must be maintained in a hydrated form during operation in order to prevent loss of ionic conduction through the electrolyte; this limits the operating temperature of the PEMFC to between 70°C and 120°C, depending on the operating pressure. The PEMFC does, however, provide much higher power density output than the other fuel cell types, and can operate efficiently at much lower temperatures. Because of this, it is envisaged that the PEMFC will find use in vehicular power generation and small-scale residential power generation applications. In particular, vehicle zero-emission regulations have been passed in areas of the United States that are likely to restrict the use of the combustion engine in the future. Pre-commercial PEMFC-powered buses and prototype PEMFC-powered vehicles are now being demonstrated for these applications.

Due to the relatively low operating temperatures of these systems, the oxidation and reduction reactions require the use of catalysts in order to proceed at useful rates. Catalysts which promote the rates of electrochemical reactions, such as oxygen reduction and hydrogen oxidation in a fuel cell, are often referred to as electrocatalysts. Precious metals, in particular platinum, have been found to be the most efficient and stable electrocatalysts for all low-temperature fuel cells operating below 300°C. The platinum electrocatalyst is provided as very small particles (~20-50Å) of high surface area, which are often, but not always, distributed on and supported by larger macroscopic conducting carbon particles to provide a desired catalyst loading.

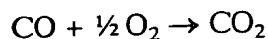
Conducting carbons are the preferred materials to support the catalyst. The electrodes include electrocatalyst material and should be designed to enhance contact between the reactant gas (*ie* hydrogen or oxygen), the electrolyte and the precious metal electrocatalyst. The electrode is porous and is often known as a gas diffusion (or gas porous) electrode. It allows the reactant gas to enter the electrode from the face of the electrode exposed to the reactant gas stream (back face); the electrolyte to penetrate through the face of the electrode exposed to the electrolyte (front face); and products, particularly water, to diffuse out of the electrode. In the PEMFC, the electrodes are bonded to the solid polymer electrolyte, which is in the form of a thin membrane, to form a single integral unit known as the membrane electrode assembly (MEA).

In most practical fuel cell systems, the hydrogen fuel is produced by converting a hydrocarbon-based fuel (such as methane) or an oxygenated hydrocarbon fuel (such as methanol) to hydrogen in a process known as reforming. This fuel, referred to as reformat, contains (in addition to hydrogen) high levels of carbon dioxide ( $\text{CO}_2$ ), of around 25%, and small amounts of impurities such as carbon monoxide (CO), typically at levels of around 1%. For fuel cells operating at temperatures below  $200^\circ\text{C}$ , and especially for the PEMFC operating at temperatures around  $100^\circ\text{C}$ ; it is well known that CO, even at levels of 1-10ppm, is a severe poison for the platinum electrocatalysts present in the electrodes. This leads to a significant reduction in fuel cell performance, *ie* the cell voltage at a given current density is reduced. This deleterious effect is more pronounced in PEMFCs operating at lower temperatures. In addition, it has been found that the  $\text{CO}_2$  present in the fuel stream can also cause a loss of performance. This performance decay is usually small compared to the effect of CO.

Various methods have been employed to alleviate anode CO poisoning. For example, reformer technology has been redesigned to include an additional catalytic reactor, known as a preferential or selective oxidation reactor. This involves the injection of air or oxygen into the hydrogen-containing reactant gas stream, prior to it passing over the selective oxidation catalyst, to oxidise the CO to  $\text{CO}_2$ . This can reduce the levels of CO from 1-2% down to below 100ppm. However, even at these levels, the anode electrocatalyst in the PEMFC is still poisoned.



It has also been found that poisoning of the electrocatalyst by CO at levels of 1-100ppm can be reduced by the use of an oxygen or air bleed directly into the anode gas stream just before it enters the anode chamber of the fuel cell itself. This is described by Gottesfeld and Pafford in J. Electrochem. Soc., 135, 2651 *et seq* (1988). This technique is believed to have the effect of oxidising the residual CO in the fuel to CO<sub>2</sub>, the reaction being catalysed by electrocatalyst sites present in the anode:



This technique provides fuel cell performance that is much closer to the performance observed when no CO is present in the fuel stream. However, the air bleed technique does not usually improve the deleterious effects of CO<sub>2</sub> on performance and there are concerns over the long-term sustainability of the cell performance when this approach is employed. This is particularly the case if high levels of air bleed, equivalent to 4% and above of the total reformat fuel volume, are required.

However, the preferred technique for alleviating fuel cell performance reduction due to anode CO poisoning is to employ an anode electrocatalyst that is itself more poison-tolerant, but which still functions as a hydrogen oxidation catalyst in the presence of CO. As described by, for example, Niedrach *et al* in Electrochem. Technol., 5, 318, (1967), the use of a bimetallic anode electrocatalyst comprising platinum/ruthenium, rather than the more conventionally-used mono-metallic platinum-only electrocatalyst, shows a reduction in the poisoning effect of the CO at typical PEMFC operating temperatures. However, again, it was not possible fully to attain the performance observed on pure hydrogen, *ie* in the absence of CO in the fuel stream, by using this approach in isolation.

There have been a number of attempts to improve the performance of anode electrocatalysts operating in the presence of hydrogen fuels containing CO. These have taken the approach of modifying existing state-of-the-art catalysts, such as combining platinum/ruthenium with other components. In 1995, Chen *et al* (J. Electrochem. Soc., 142, (10)) discussed the need to develop CO-tolerant catalysts and studied the

oxidation of impure  $H_2$  on Teflon<sup>®</sup>-bonded carbon-supported platinum/ruthenium/ tungsten oxide electrodes. The use of tungsten oxide ( $WO_3$ ) as a promoter of improved activity of platinum catalysts towards impure  $H_2$  was not new. As far back as 1965, it was known that tungsten oxides were effective in promoting the electro-oxidation of CO on platinum-containing electrodes in acid-electrolyte fuel cells (Niedrach and Weinstock, *Electrochem. Technol.*, 3, 270-5 (1965)). A more recent example of a catalyst having improved CO tolerance is given in European patent specification no. EPA 838 872.

EPA 838 872 relates to a ternary catalyst comprising Pt-M-Y, wherein Pt-M is an alloy of platinum and one or more metals selected from the transition metal elements or from Groups IIIA or IVA of the Periodic Table in "Handbook of Chemistry and Physics" 64th Edition, CRC Press, and Y is a bronze-forming element or an oxide thereof, characterised in that the Pt-M alloy is in intimate contact with Y, and provided that M is not Ru if Y is  $WO_3$ .

However, such electrocatalysts aimed at improving CO tolerance apparently do not also have the effect of improving performance when  $CO_2$  is present in the reformat fuel. Hence, for example, in the case of certain materials described in EPA 838 872, improved CO tolerance is observed, but at the same time the presence of  $CO_2$  in the reformat stream causes larger performance losses than those observed with state-of-the-art alloys of platinum and ruthenium. This behaviour is most likely due to the CO tolerance mechanism for the catalysts described in EPA 838 872 differing from that observed with Pt/Ru alloys.

We have now surprisingly found that significant improvement in both CO and  $CO_2$  tolerance can be achieved by providing an electrode in which the state-of-the-art Pt/Ru-type electrocatalyst is associated with a second electrocatalyst, such as one chosen from the ternary catalysts described in EPA 838 872.

Accordingly, the present invention provides an electrode, which may be an anode or cathode, comprising a first catalytic component and a second catalytic component,

characterised in that the first catalytic component comprises one or more electrocatalyst(s) of formula  $\text{Pt-M}_m\text{-Y}$  and the second catalytic component comprises one or more electrocatalyst(s) of formula  $\text{Pt-M}_m$ .

- 5 In these formulae, Pt represents platinum, m is 0 or a number greater than 0, and, when greater than 0,  $\text{Pt-M}_m$  is an alloy. The  $\text{Pt-M}_m$  alloy is preferably more than a mere physical mixture of Pt with metal(s) M, since the platinum and metal(s) M are preferably heat-treated to promote a measurable interaction between the platinum and metal(s) M to change the intrinsic properties of the platinum metal. Heat-treatment
- 10 causes a significant number of atoms of the metal(s) M to be incorporated into the atomic crystal lattice, or unit cell, of the platinum particle. This process usually distorts the dimensions of the platinum unit cell, since the atoms of the metal(s) M will generally be of a different size from those of the platinum, and this can usually be measured by techniques such as X-ray diffraction. The characteristic dimensions of the
- 15 platinum unit cell, referred to by crystallographers as the lattice parameter, can be shown to have altered due to the fact that two or more metals, with different atomic sizes, have been incorporated into a single, homogeneous metal alloy particle at the atomic level.
- 20 Preferably, the one or more metals(s) M, when present, is or are selected from the groups IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA or IVA of the Periodic Table in "Handbook of Chemistry and Physics" 64th Edition, CRC Press; for example, from the group Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf and Sn; especially Ru, Mn, CO, Ni and Rh. In addition,  $\text{Pt-M}_m$  also includes pure platinum (*ie*  $m = 0$ ) for the purpose of
- 25 this invention.

Furthermore, in the first catalytic component, the  $\text{Pt-M}_m$  alloy is in intimate contact with component Y. By the term "intimate contact" is meant that component Y may either be alloyed with the  $\text{Pt-M}_m$  alloy (the resulting alloy being as defined

30 hereinbefore) or may be unalloyed but in physical contact with the alloy. Component Y may be a bronze-forming element or an oxide thereof. A 'bronze' material is defined by Wold and Dwight in Solid State Chemistry - Synthesis, Structure, and Properties of

Selected Oxides and Sulfides, Chapman & Hall as "... an oxide with intense colour (or black), having a metallic lustre and showing either semi-conducting or metallic behaviour. A principle characteristic of bronzes is their range of composition, which results in the transition metal exhibiting a variable formal valence." Suitable bronzes include non-stoichiometric alloys of the transition metal with hydrogen.

The component Y is suitably selected from one or more of the Group IVB to VIB elements and rhenium or an oxide thereof, for example Ti, V, Nb, Ta, Mo, W, Re, or an oxide thereof; suitably Ti, V, Ta, Mo, W, or an oxide thereof; preferably Mo or W, or an oxide thereof.

The first catalytic component may therefore be chosen from one described in EPA 838 872. Preferably, the first catalytic component is one wherein the Pt-M<sub>m</sub> is Pt (alone) or an alloy (as defined) of Pt/Ru, Pt/Co or Pt/Ti, further alloyed or in physical contact with Mo or W, or an oxide thereof such as WO<sub>3</sub>.

Preferably, the second catalytic component is one wherein the Pt-M<sub>m</sub> is Pt (alone) or an alloy (as defined) of Pt/Ru.

The electrode of the present invention shows improved tolerance to both CO and CO<sub>2</sub> poisons whilst maintaining high activity for the desired electrochemical reaction, and is therefore of use as either the anode or the cathode in fuel cells which use an impure feed. The electrode may be of benefit in both phosphoric acid and solid polymer fuel cells. Specifically, it shows tolerance to both CO and CO<sub>2</sub> poisons in reformat fuel and is therefore specifically of use as an anode.

The invention further provides the use of an electrode of the invention in an electrochemical device. Suitably, the electrochemical device is an MEA. Suitably, the use is as a fuel cell anode.

The invention will now be described further with reference to the following examples.

### COMPARATIVE EXAMPLE 1

A catalyst containing platinum and ruthenium supported on Cabot Vulcan XC72R carbon, such that the nominal platinum loading is 40 wt%, and the nominal ruthenium loading is 20 wt% (atomic ratio 50:50), was prepared using a process comprising the deposition of Pt onto the conductive carbon black substrate by the hydrolysis of a soluble Pt salt by a base in the presence of the carbon black, as disclosed in EP 450 849. From this catalyst a catalyst ink was prepared and a fuel cell anode was printed onto pre-teflonated Toray TPG90 paper. Inks and electrodes are prepared as detailed in Example 2 of European patent specification no. EPA 731 520.

### COMPARATIVE EXAMPLE 2

A catalyst containing platinum, ruthenium and tungsten oxide was prepared. PtRu catalyst (7.5g), prepared according to Comparative Example 1 at 19.2 wt% Pt and 9.1 wt% Ru loading supported on Cabot Vulcan XC72R, was slurried in 1 litre demineralised water for one hour. A 1 wt% solution of sodium tungstate in demineralised water was prepared containing 1.98g tungsten. This solution was converted to tungstic acid by passing it through an exchange column, comprising Dowex 50-X8 ion-exchange resin, and fed directly into the slurry. The resultant catalyst was stirred overnight and then filtered, dried at 105°C in air and fired at 500°C in a gas mixture containing 6%CO in CO<sub>2</sub>. An electrode containing this catalyst was prepared in the same way as described in Comparative Example 1.

### COMPARATIVE EXAMPLE 3

A catalyst containing Pt, Mo and Co with an atomic ratio of 66:20:15 was prepared. To a stirred suspension of Cabot Vulcan XC72R carbon in a solution of sodium hydrogen carbonate under reflux, was added a solution of chloroplatinic acid sufficient to give a loading of 20% platinum. The resulting slurry was filtered, and washed with demineralised water until no chloride was detectable in the washings. The catalyst was dried at 100°C in air. The catalyst was re-slurried in hot sodium hydrogen carbonate

solution and a solution of cobalt dichloride was added dropwise. The ratio of alkali to metal salts for both steps was such as to ensure complete hydrolysis and precipitation of the metal hydrous oxides/hydroxides onto the carbon.

- 5 The slurry was filtered, and washed with demineralised water until no chloride was detectable in the washings. The wet cake was then dispersed in demineralised water. To this slurry was added a solution of molybdenum. This was prepared by the dissolution of molybdenum powder in hydrogen peroxide solution, followed by decomposition of the excess peroxide by platinum black. The combined slurry was
- 10 then evaporated to dryness. The resulting catalyst was then heated at 650°C in flowing 5% hydrogen in nitrogen to ensure reduction and alloying of the components. X-ray diffraction analysis of the fired catalyst showed a single cubic phase indicating full alloying of the three components.
- 15 An electrode containing this catalyst at a platinum loading of 0.4mgPt/cm<sup>2</sup> was prepared as described in Comparative Example 1.

#### EXAMPLE 1 - (Pt/Mo/Co)/(Pt/Ru)

- 20 A catalyst containing Pt, Mo and Co with an atomic ratio of 66:20:15 was prepared as described in Comparative Example 3.

An electrode containing this catalyst at a platinum loading of 0.26mgPt/cm<sup>2</sup> was prepared as described in Comparative Example 1. On top of this catalyst layer, an

25 additional layer of PtRu catalyst made according to Comparative Example 1 was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.14mgPt/cm<sup>2</sup>.

#### EXAMPLE 2 - (Pt/W/Co)/(Pt/Ru)

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A catalyst containing Pt, W and Co with an atomic ratio of 66:20:14 was prepared. First, a PtCo catalyst was prepared as described in Comparative Example 3. The wet

cake of this catalyst was then dispersed in demineralised water. To this slurry was added a solution of tungsten. This was prepared by the dissolution of tungsten powder in hydrogen peroxide solution, followed by decomposition of the excess peroxide by platinum black. The combined slurry was evaporated to dryness. The resulting catalyst was then heated at 900°C in flowing nitrogen to ensure reduction and alloying of the components. X-ray diffraction analysis of the fired catalyst showed a single cubic phase indicating full alloying of the three components.

An electrode containing this catalyst at a platinum loading of 0.27mgPt/cm<sup>2</sup> was prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of PtRu catalyst made according to Comparative Example 1 was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.24 mgPt/cm<sup>2</sup>.

#### EXAMPLE 3 - (Pt/Ru/WO<sub>3</sub>)/(Pt/Ru)

A catalyst containing Pt, Ru and tungsten oxide was prepared as described in Comparative Example 2.

An electrode containing this catalyst at a platinum loading of 0.12mgPt/cm<sup>2</sup> was prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of PtRu catalyst made according to Comparative Example 1 was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.25mgPt/cm<sup>2</sup>.

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#### EXAMPLE 4 - (Pt/Ti/W)/(Pt/Ru)

A catalyst containing Pt, Ti and W with an atomic ratio of 65:15:20 was prepared. To a stirred suspension of Cabot Vulcan XC72R carbon in a solution of sodium hydrogen carbonate under reflux, was added a solution of chloroplatinic acid sufficient to give a loading of 40% platinum. The resulting slurry was filtered, and washed with demineralised water until no chloride was detectable in the washings. The catalyst was

dried at 100°C in air. The catalyst was re-slurried in hot sodium hydrogen carbonate solution and a solution of titanium trichloride and urea was added dropwise. The ratio of alkali to metal salts for both steps was such as to ensure complete hydrolysis and precipitation of the metal hydrous oxides/hydroxides onto the carbon.

5

The slurry was filtered, and washed with demineralised water until no chloride was detectable in the washings. The wet cake was then dispersed in demineralised water. To this slurry was added a solution of tungsten. This was prepared by the dissolution of tungsten powder in hydrogen peroxide solution, followed by decomposition of the excess peroxide by platinum black. The combined slurry was then evaporated to dryness. The resulting catalyst was then heated at 650°C in flowing 5% hydrogen in nitrogen to ensure reduction and alloying of the components.

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An electrode containing this catalyst at a platinum loading of 0.16mgPt/cm<sup>2</sup> was prepared as described in Comparative Example 1. On top of this catalyst layer, an additional layer of PtRu catalyst made according to Comparative Example 1 was applied using the method described in Comparative Example 1. The additional Pt loading in this catalyst layer was 0.13mgPt/cm<sup>2</sup>.

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#### EXAMPLE 5 - PREPARATION OF MEAs

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The selected anode is formed into an MEA. The electrodes of the MEAs were prepared as described in Example 2 of EP 731 520. The MEA was fabricated by hot-pressing the anode and a pure platinum catalyst cathode (with a platinum loading of 0.6mg Pt/cm<sup>2</sup>) against each face of a solid proton-conducting electrolyte membrane. The membrane used was the perfluorinated membrane Nafion® 115 (from Du Pont de Nemours). MEAs of 6.5cm<sup>2</sup> area were formed by hot-pressing at pressures of 100 psi (1 psi = 6.89 x 10<sup>3</sup> N/m<sup>2</sup>) over the MEA, at temperatures exceeding the glass transition temperature of the membrane, as is commonly practised in the art.

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## EXAMPLE 6 - PERFORMANCE EVALUATION

The MEAs were evaluated in a PEMFC single cell which consists of graphite plates into which flowfields are machined to distribute the reactant gases, and to remove products. The MEA was located between the appropriate flowfield plates. The cell was held together by two copper plates and compressed by tightening four stainless steel bolts in the corners of these plates using a torque spanner at 7Nm. The cell was heated using two cartridge heaters inserted into the copper plates. Gases were humidified using two membrane humidifiers operated at 75°C and passed to the cell through tubing heated to 90°C.

The "fuel cell performance" was assessed by measuring the voltage and current density relationship. The fuel cell operated under conditions representative of those employed in practical PEM fuel cells. These conditions were typically a reactant gas inlet temperature of 80°C, a pressure of both hydrogen and air reactants of 3 atmospheres. The reactant gas streams were kept constant at 0.1SLPM (standard litres at 1 bar and 0°C per minute); 0.125 SLPM for 25% CO<sub>2</sub> and 75% hydrogen; and 0.4 SLPM for oxygen. For the single cell reformate tolerance experiments, the anode gas stream was changed at time t=0 from pure hydrogen to hydrogen with 100ppm of CO or to a stream containing 25% CO<sub>2</sub> and 75% hydrogen. At constant current density of 0.5 Acm<sup>-2</sup>, the cell potential was then monitored with time in order to assess the CO and the CO<sub>2</sub> tolerance of different catalysts under practical conditions.

Figure 1 shows fuel cell performance data of cell voltage vs time for operation of PtRu, PtRuWO<sub>3</sub> and PtMoCo catalysts in a gas stream containing 25% CO<sub>2</sub> and 75% hydrogen. The anode platinum loadings are respectively 0.37, 0.29 and 0.40 mg Pt/cm<sup>2</sup>. Figure 1 shows that the single cell voltages for the three MEAs employing PtRu, PtRuWO<sub>3</sub> and PtMoCo catalysts decay from their value at t=0 min when the cell is operated with pure hydrogen. The performance of the electrodes containing PtRuWO<sub>3</sub> and PtMoCo degrades by over 50 mV on introduction of the gas mixture containing 25% CO<sub>2</sub> and 75% hydrogen. The current state-of-the-art CO<sub>2</sub> tolerant catalyst, PtRu, decays by approximately 20 mV.

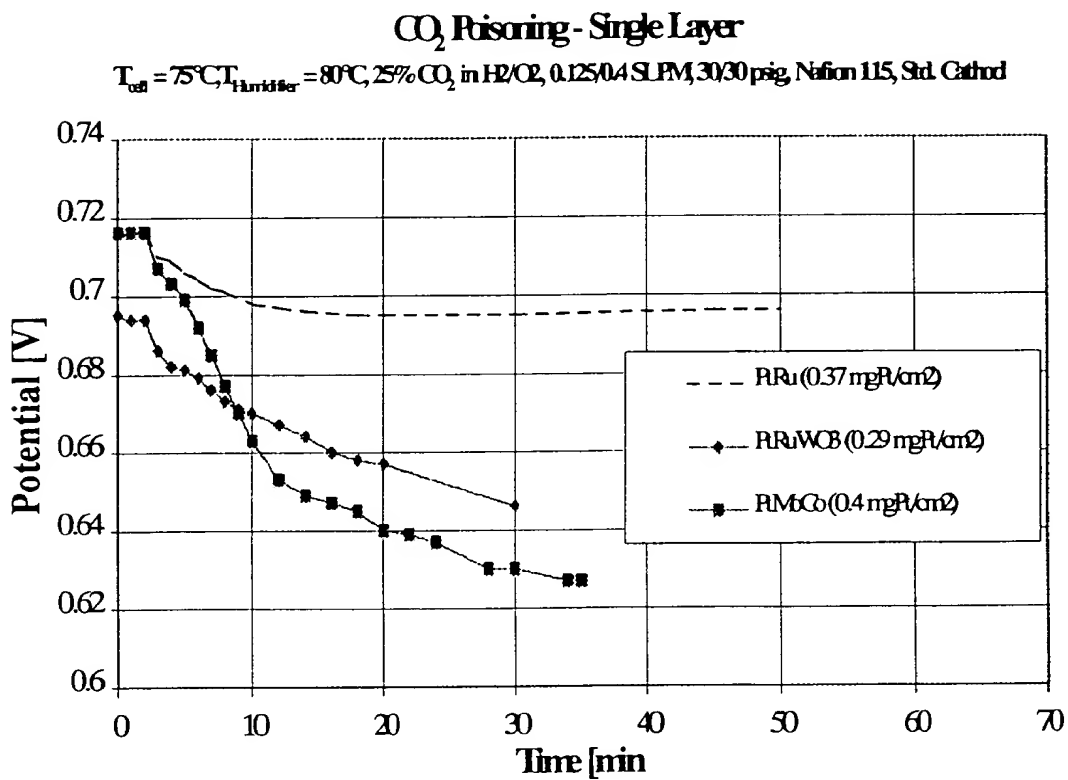
Figure 2 presents single cell performance data for electrode bilayers according to the invention operating in 25% CO<sub>2</sub> and 75% hydrogen. The bilayers comprise of catalyst layers of PtTiW, PtRuWO<sub>3</sub> and PtMoCo containing 0.16, 0.12 and 0.26 mg Pt cm<sup>-2</sup> and layers of PtRu catalyst at loadings of 0.13, 0.25 and 0.14 mg Pt cm<sup>-2</sup>, respectively. Figure 2 also shows the comparative sample PtRu which is also presented in Figure 1. The bilayer catalysts according to the invention show small decays when the gas stream is changed at t=0 min from pure hydrogen to 25%CO<sub>2</sub> and 75% hydrogen. The performance decay of the PtRuWO<sub>3</sub> sample when a bilayer shows a significant reduction. The other electrode samples exhibit a decay around 20 mV, very close to the comparative PtRu electrode.

Figure 3 shows that, at the same time, the performance of the bilayer electrodes of the invention in hydrogen containing 100 ppm CO is significantly improved over the comparative PtRu sample. When at t=0 min the gas stream is changed from pure hydrogen to hydrogen containing 100 ppm CO, all samples exhibit, after some induction time, a decay of the single cell voltage. This decay is 160 mV for the comparative PtRu sample. All bilayer samples show lower performance decay, while the total platinum loading in both layers is very similar in all cases. The PtMoCo/PtRu bilayer electrode of the invention shows a performance decay as low as approximately 85 mV.

Clearly, the bilayer approach according to the invention has improved the performance decay of the catalysts studied in 25%CO<sub>2</sub> and 75% hydrogen, and has improved the performance in hydrogen streams containing 100 ppm CO. The bilayers according to the invention therefore show good CO<sub>2</sub> and very good CO tolerance.

FIGURE 1: CO<sub>2</sub> POISONING - COMPARATIVE DATA

Performance degradation of prior art electrocatalysts at  $0.5 \text{ A cm}^{-2}$  in gas stream containing 25%CO<sub>2</sub> and 75%H<sub>2</sub>.

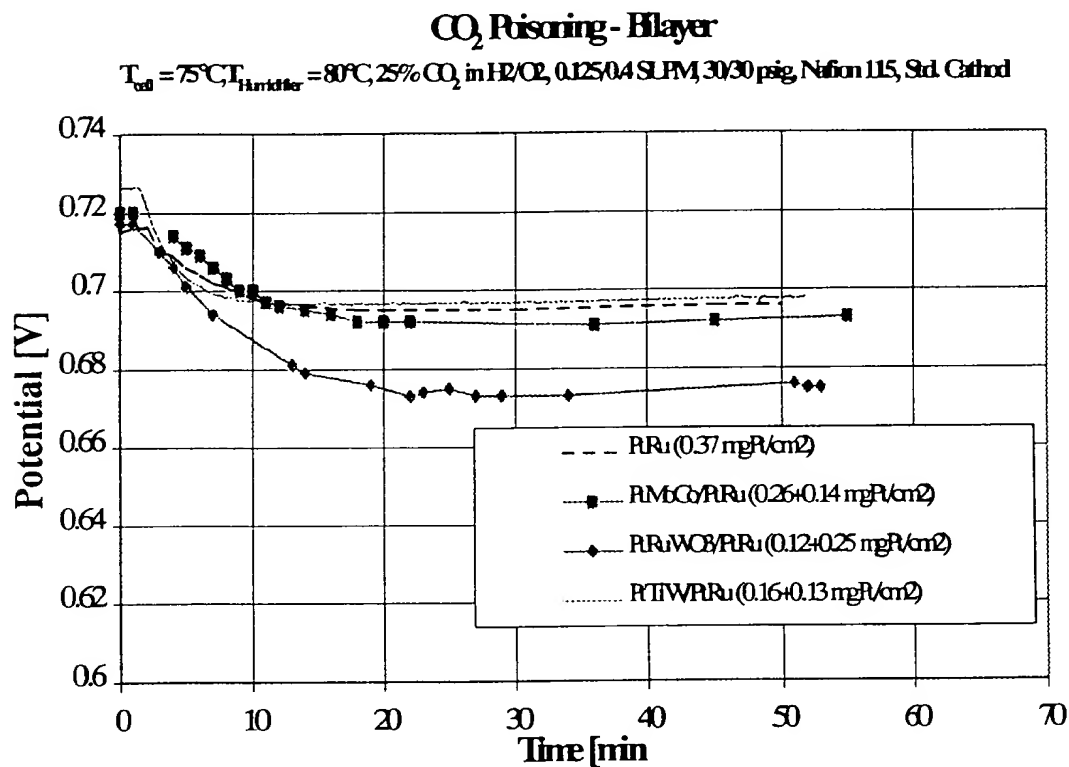


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FIGURE 2: CO<sub>2</sub> POISONING – BILAYER

Performance degradation at  $0.5 \text{ A cm}^{-2}$  in gas stream containing 25% CO<sub>2</sub> and 75% H<sub>2</sub>.  
In a bilayer configuration with PtRu, the performance vs CO<sub>2</sub> is very similar to PtRu.

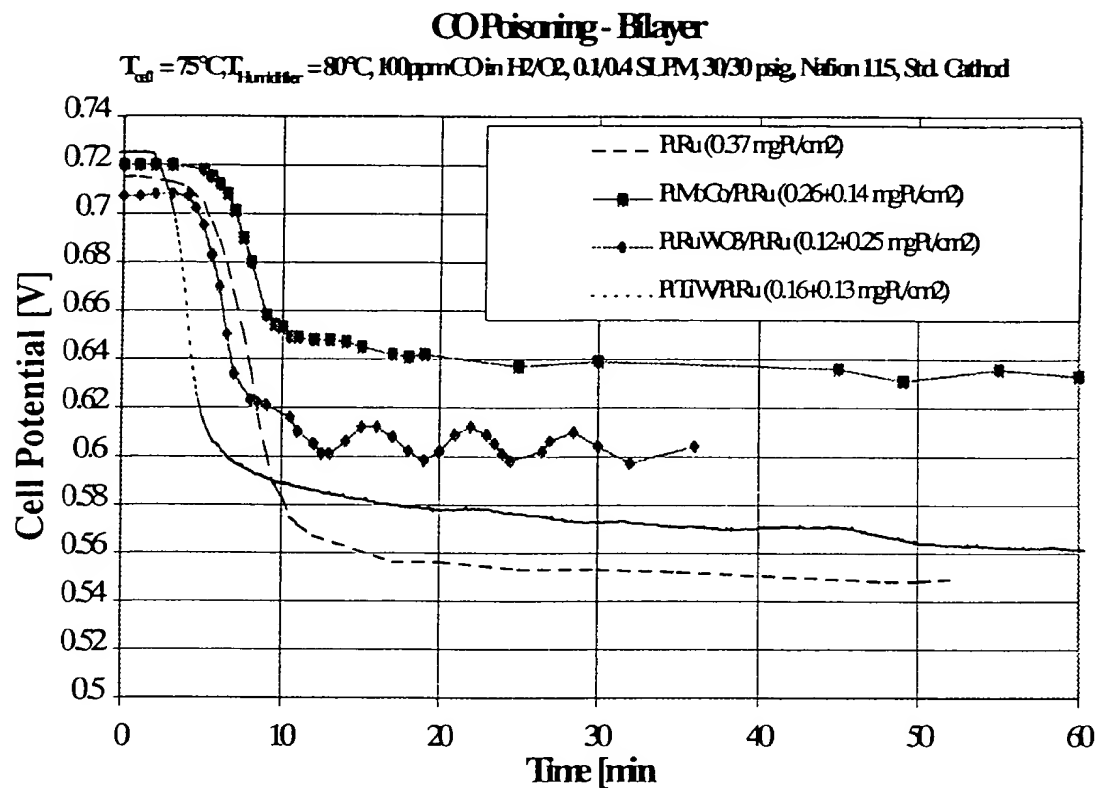
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FIGURE 3: CO POISONING - BILAYER

Performance degradation at  $0.5 \text{ A cm}^{-2}$  in a hydrogen gas stream containing 100ppm CO. In a bilayer configuration with PtRu, the electrode performance vs CO is superior to a comparative PtRu electrode.



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Johnson Matthey Tee cont.